

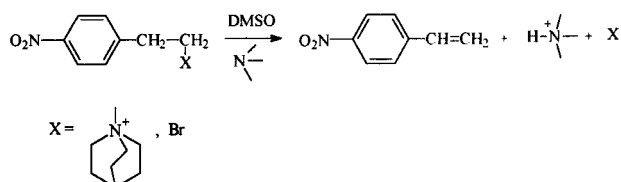
# A study on the $\beta$ -elimination reaction from N-[2-(*p*-nitrophenyl)ethyl]quinuclidinium and 2-(*p*-nitrophenyl)ethyl bromide induced by amines in dimethylsulfoxide with formation of *p*-nitrostyrene<sup>†</sup>

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Second order rate constants  $k_E$  M<sup>-1</sup> s<sup>-1</sup> for the  $\beta$ -elimination reaction from N-[2-(*p*-nitrophenyl)ethyl]quinuclidinium and 2-(*p*-nitrophenyl)ethyl bromide induced by amines of different structure in dimethylsulfoxide at 50 °C have been measured. Application of the Brønsted equation shows a similar behaviour of the two substrates, with values of  $\rho = 0.649$  and 0.584 respectively.

Distinguishing between a concerted E<sub>2</sub> or a step-wise E<sub>1</sub>cb irreversible mechanism (E<sub>1</sub>cb)<sub>1</sub> of elimination reactions is a difficult task.<sup>1–3</sup> It has been demonstrated<sup>4,5</sup> that the base-induced  $\beta$ -elimination from N-[2-(*p*-nitrophenyl)ethyl]quinuclidinium in H<sub>2</sub>O follows an E<sub>1</sub>cb reversible mechanism, (E<sub>1</sub>cb)<sub>R</sub>; however, the addition of the dipolar aprotic solvent DMSO, decreases the degree of reversibility of the formation of the intermediate carbanion, and when the percentage of DMSO reaches 60% vol, an E<sub>1</sub>cb irreversible mechanism, (E<sub>1</sub>cb)<sub>1</sub> is observed<sup>6</sup>. It is therefore reasonable to assume that in 100% DMSO, the base-induced  $\beta$ -elimination from this substrate follows an (E<sub>1</sub>cb)<sub>1</sub> mechanism. In our study, we have compared the dependence of the reactivity of N-[2-(*p*-nitrophenyl)ethyl]quinuclidinium (1) with that of 2-(*p*-nitrophenyl)ethyl bromide (2) on a series of amines with different structures at 50 °C in DMSO. Both processes lead to the formation of *p*-nitrostyrene, scheme 1:



Scheme 1

The mechanism of the base-induced  $\beta$ -elimination reaction from (2) has been assigned<sup>6</sup> as concerted E<sub>2</sub> based on the structure-reactivity interactions. It has been reported<sup>7–9</sup> that some proton transfer reactions from carbon acids catalysed by amines of different structures, can show different behaviours in a Brønsted plot,<sup>10,11</sup> depending on the structure of the amine; these deviations have been related to the structure of the transition state of the process. It is of interest to compare the reactions of the two substrates, (1) and (2), which are reported to react by the two different mechanisms, E<sub>2</sub> or (E<sub>1</sub>cb)<sub>1</sub> respectively, and to study their behaviour with respect to the structure of the amine catalysts.

Kinetic studies were carried out in pseudo first-order conditions, with an excess of amine with respect to the substrate. The formation of *p*-nitrostyrene in DMSO at 50 °C was followed at  $\lambda = 336$  nm. Most of the reactions were followed to completion; the slower reactions were followed by initial rates. The elimination reactions are of second order with all amines, first order with respect to the substrate and first order

**Table 1** Second-order rate constants,  $k_E$  M<sup>-1</sup> s<sup>-1</sup> for elimination reactions from N-[2-(*p*-nitrophenyl)ethyl]quinuclidinium (1) and 2-(*p*-nitrophenyl)ethyl bromide (2) induced by amines in DMSO at 50 °C or 25 °C

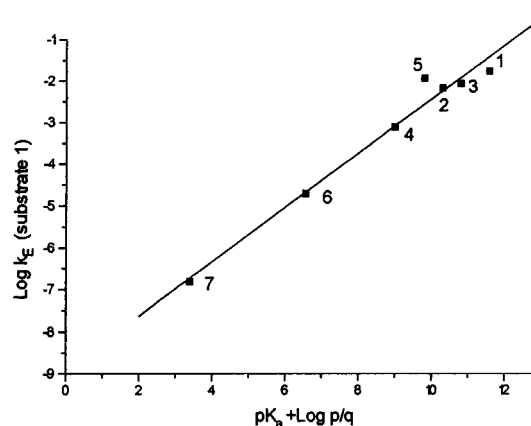
Amine	10 <sup>3</sup> $k_E^a$ M <sup>-1</sup> s <sup>-1</sup>	10 <sup>2</sup> $k_E^b$ M <sup>-1</sup> s <sup>-1</sup>	10 <sup>2</sup> $k_E^c$ M <sup>-1</sup> s <sup>-1</sup>	pK <sub>a</sub> <sup>d</sup>	(pK <sub>a</sub> +log p/q) <sup>e</sup>
1-Butylamine (1)	16.8	8.04	2.1	11.1 <sup>(15)</sup>	11.57
Dibutylamine (2)	6.48	5.89	1.8	10.0 <sup>(15)</sup>	10.3
Diethylamine (3)	8.45	9.50	2.4	10.5 <sup>(15)</sup>	10.8
Triethylamine (4)	0.745	1.3	0.33	9.0 <sup>(15)</sup>	9.0
Quinuclidine (5)	11.2	27.8	7.15	9.8 <sup>(17)</sup>	9.8
Imidazole (6)	0.0196	0.0184	0.0026	6.26 <sup>(18)</sup>	6.56
Pyridine (7)	0.000154	0.00051		3.4 <sup>(15)</sup>	3.4

<sup>a</sup>substrate (1) at 50 °C; <sup>b</sup>substrate (2) at 50 °C; <sup>c</sup>substrate (2) at 25 °C; <sup>d</sup>the pK<sub>a</sub> of the conjugate acid of the amine are at 25 °C in DMSO. <sup>e</sup> $\rho$  is the number of equivalent protons in the conjugate acid of the amine,  $q$  is the number of basic nitrogen in the amine.

with respect to the amine. The first order kinetics with all amines, excludes the possibility of catalysis by a second molecule of amine in the transition state: this possibility has been reported.<sup>12</sup> An (E<sub>1</sub>cb)<sub>R</sub> mechanism can also be excluded because it is not compatible with the result of second order kinetics. In Table 1 the measured second order rate constants,  $k_E$  M<sup>-1</sup> s<sup>-1</sup>, are reported for the amine-induced  $\beta$ -elimination from (1) and (2) in DMSO at 50 °C or 25 °C.

Figures 1, 2 and 3 show the related Brønsted plots.

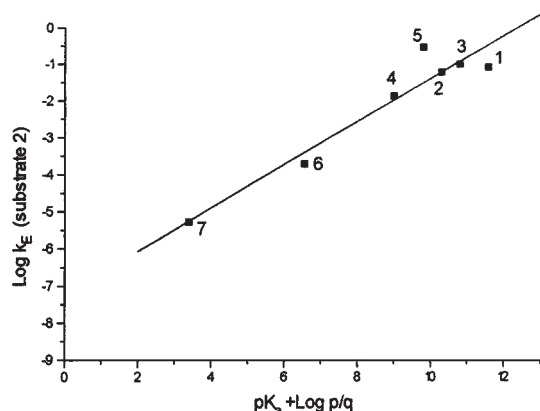
From Figs 1, 2 and 3, it can be seen that the different classes



**Fig. 1** Brønsted plot for the  $\beta$ -elimination reactions induced by amines from N-[2-(*p*-nitrophenyl)ethyl]quinuclidinium (1) in DMSO at 50 °C. Linear regression analysis gives the equation:  $y = -8.93 + 0.649x$ ,  $r = 0.9870$ . Numbers on the plot refer to amines as in Table 1.

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<sup>†</sup> This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.



**Fig. 2** Brønsted plot for the  $\beta$ -elimination reactions induced by amines from 2-(*p*-nitrophenyl)ethyl bromide (**2**) in DMSO at 50°C. Linear regression analysis gives the equation:  $y = -7.24 + 0.584x$ ,  $r = 0.9602$ . Numbers on the plot refer to amines as in Table 1.

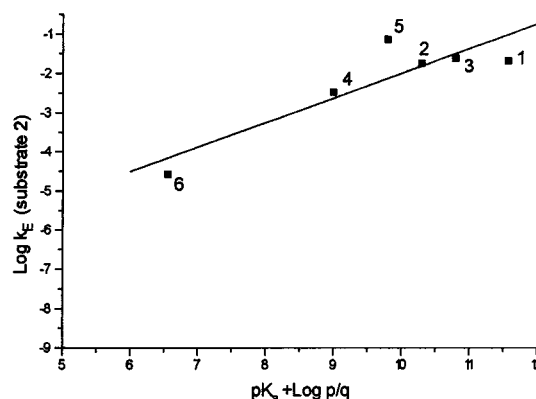
of amines follow the same linear correlation and steric effects due to the structure of the amine are not relevant. In all cases, quinuclidine was found to be slightly more reactive than predicted from the Brønsted equation. Also, no curvatures are observed within the three plots, even if there is a large variation in the  $pK_a$  of the amines used. The behaviour of the two substrates, (**1**) and (**2**) on the Brønsted plot is very similar, with a  $\beta$  value of 0.649 (**1**) and 0.584 (**2**) at 50°C. It can be concluded that the two mechanisms,  $(E_1cb)_1$  in which rate determining is proton transfer, (substrate **1**), or  $E_2$ , in which proton transfer is coupled with carbon-leaving group bond breaking, (substrate **2**), do not show significant differences in a Brønsted plot with respect to the amine catalyst.

It has been estimated<sup>5</sup> for the  $pK_a$  of (**1**) in DMSO a value of  $pK_a = 16$  (acidic proton in the  $\beta$  position with respect to the quinuclidinium group). From the Brønsted plot of Fig. 1 a value for the intrinsic rate constant<sup>13</sup> can be estimated:  $\log k_0 = 1.45$  ( $k_0$  is the extrapolated rate constant with a catalyst of  $pK_a = 16$ ). This value is consistent with reported<sup>13</sup> values of intrinsic rate constants for carbanion-forming reactions from carbon acid. A value for the intrinsic barrier,<sup>11,13</sup> as defined by Marcus,<sup>14</sup> can then be calculated:  $\Delta G_0^\ddagger = 15.67$  kcal/mol. This significant value of  $\Delta G_0^\ddagger$  for the process from substrate (**1**) can explain<sup>11</sup> the lack of curvature in the Brønsted plot of Fig. 1. Also, the significant value of  $\Delta G_0^\ddagger$  can be related to the "principle of imperfect synchronisation",<sup>15,16</sup> in this case there would be a lack of synchronisation, in the transition state, in the stabilisation of the negative charge of the intermediate carbanion by the *p*-nitrophenyl group.

In conclusion the two substrates, (**1**) or (**2**), reacting by a  $\beta$ -elimination reaction in DMSO with two different mechanisms  $(E_1cb)_1$  or  $E_2$  respectively present a similar behaviour in a Brønsted plot with amine catalyst of different structures. This technique therefore cannot be used to distinguish the two processes.

## Experimental

N-[2-(*p*-nitrophenyl)ethyl]quinuclidinium (**1**) was prepared following the procedure previously described.<sup>4</sup> 2-(*p*-nitrophenyl)ethyl bromide (**2**), (Aldrich) was recrystallized twice before use. DMSO was first dried over 4 Å molecular sieves and then distilled *in vacuo* from calcium hydride at 50°C. All the amines used were commercial. The liquid amines were redistilled, while the solid amines were recrystallised.



**Fig. 3** Brønsted plot for the  $\beta$ -elimination reactions induced by amines from 2-(*p*-nitrophenyl)ethyl bromide (**2**) in DMSO at 25°C. Linear regression analysis gives the equation:  $y = -8.26 + 0.626x$ ,  $r = 0.8885$ . Numbers on the plot refer to amines as in Table 1.

## Kinetics

The formation of *p*-nitrostyrene was followed at  $\lambda = 336$  nm, ( $\epsilon = 6581$  M<sup>-1</sup> cm<sup>-1</sup> in DMSO at 50°C). Reactions were studied in conditions of pseudo first order, an excess of amine in all cases being used. Second order rate constants,  $k_E$  M<sup>-1</sup> s<sup>-1</sup>, were always found to be independent of amine concentration. Most of the reactions were followed to completion and the second order rate constant was calculated from

$\ln(A_\infty - A_0)/(A_\infty - A_t) = k_E t [\text{amine}]$ . The slower reactions were followed by initial rates<sup>4</sup> and  $k_E$  calculated from the equation:  $A_t = A_0 + k_E t [\text{amine}] (A_\infty - A_0)$ . Some processes of intermediate reactivity were followed with both methods and the calculated second-order rate constants were found to be in agreement within  $\pm 5\%$ . The values of  $k_E$  M<sup>-1</sup> s<sup>-1</sup> were taken as the average of the values measured at several amine concentrations. The range of amine concentration was between 0.01 and 0.1 M; with imidazole 0.1–0.4 M and with pyridine 0.4–0.8 M.

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